points within each run; it was always less than 6% and averaged 3.6% for the runs in this Table. Check runs with different initial concentrations of reactants were generally done, and gave average rate constants averaging within 3.5% of the corresponding runs reported in Table III. The rate was always found to be first order with respect to the halide and first order with respect to the nucleophilic reagent.

Table IV gives detailed data for one of these runs.

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CAMBRIDGE, MASS. RECEIVED AUGUST 1, 1950

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Copolymerization. XVII. The Over-all Rate of Copolymerization of Styrene–Diethyl Fumarate[1]

BY CHEVES WALLING[2] AND ELIZABETH A. MCELHILL

The rates of polymerization and copolymerization of styrene and diethyl fumarate have been measured in the presence and absence of 2-azobis-isobutyronitrile as initiator at 60°. The ratio of the rate constant for bimolecular crossed termination to the geometric mean of the rate constants for bimolecular termination of the individual monomers is approximately 7.75. Attempts to calculate the rate of thermal cross initiation for this monomer pair has led to anomalous results, since diethyl fumarate apparently inhibits the thermal polymerization of styrene.

An equation describing the over-all rate of copolymerization for the case of chain termination by bimolecular interaction of radicals has been developed by Melville, Noble and Watson,[3] and by Walling,[4] and may be expressed in the form

$$\frac{-\mathrm{d}([\mathrm{M}_1] + [\mathrm{M}_2])}{\mathrm{d}t} = \frac{(r_1[\mathrm{M}_1]^2 + 2[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2)I^{1/2}}{(r_1{}^2[\mathrm{M}_1]^2 + 2\phi r_1 r_2[\mathrm{M}_1][\mathrm{M}_2]\delta_2/\delta_1 + r_2{}^2[\mathrm{M}_2]^2(\delta_2/\delta_1)^2)^{1/2}} \quad (1)$$

where M's are monomer concentrations, I the rate of chain initiation, r's the monomer reactivity ratios for the monomer pair involved, and δ's the ratio of the rate constant for chain propagation to the square of the rate constant for chain termination of the individual monomers. The quantity ϕ represents the ratio of the rate constant for bimolecular cross termination to the geometric mean of the rate constants for bimolecular termination of the two monomers alone. Since all quantities but I and ϕ can be obtained from rate studies on the single monomers and measurements of copolymer compositions, and since I can be fixed, for example, by selecting an efficient chain initiator with a constant rate of decomposition such as 2-azobis-isobutyronitrile, equation (1) provides the means of determining ϕ by the measurement of over-all copolymerization rates. By this means, ϕ has been determined for the systems styrene–methyl methacrylate[4,5] and styrene–methyl acrylate.[4] In addition, it has been possible to determine as well the rate constant for cross initiation in the styrene–methyl methacrylate system.[4]

Experimental

Polymerization Technique.—Styrene was commercial material vacuum distilled before use. Diethyl fumarate came from two samples of commercial material, one fractionally distilled *in vacuo* by Mr. V. G. Simpson and the other kindly supplied by Dr. D. C. Seymour, both of this Laboratory, and having the physical constants b.p. 97° (10 mm.), $n^{20}\mathrm{D}$ 1.4416. Polymerizations were carried out on 4- or 5-ml. samples in sealed, evacuated tubes and polymer yields determined by the usual technique of polymer isolation by multiple precipitation and solution from benzene–petroleum ether followed by vacuum sublimation of solvent from a benzene solution. In the case of the thermal polymerizations, particular care was taken to exclude light by wrapping the tubes in tin foil. The rate of decomposition of 2-azobis-isobutyronitrile in diethyl fumarate was obtained by measuring the rate of nitrogen evolution with a gas buret from a solution of 1.0046 g. (6.09 millimoles) of azo compound in 15.0 ml. of diethyl fumarate in a reaction flask gently shaken in a 60° thermostat. In order to eliminate any apparent induction period brought about by absorption of oxygen by the radicals produced, air was displaced from the system by nitrogen and nitrogen bubbled through the solution for a few minutes prior to the start of the reaction.

Results and Discussion

The use of equation (1) in the treatment of over-all rates of copolymerization requires a known (preferably constant) rate of chain initiation and chain termination by a bimolecular process. In order to determine the rate of decomposition of 2-azobis-isobutyronitrile in diethyl fumarate the rate of nitrogen evolution from a solution of 2-azobis-isobutyronitrile in diethyl fumarate at 60° was measured and, in Fig. 1, the logarithm of the amount of azo compound remaining is plotted against time. The experiment was interrupted after seven hours since the polymerization of the fumarate proceeded far enough to yield a highly viscous reaction mixture, and a calculated value for the final volume of nitrogen was employed. From the data in the figure, a rate constant of 9.4 × 10^{-6} can be calculated for the decomposition of 2-azobis-isobutyronitrile. The rate constant of decomposition of 2-azobis-isobutyronitrile in xylene at 60° is approximately 1 × 10^{-5} sec.$^{-1}$, and is almost independent of the solvent used.[5a,6] Since the radicals from this initiator approach 100% efficiency in starting polymer chains, in the cases of styrene, methyl methacrylate and vinyl acetate,[4]

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[1] For the previous paper in the copolymerization series see K. W. Doak, D. L. Dineen, THIS JOURNAL, **73**, 1084 (1951).

[2] Lever Brothers Company, 164 Broadway, Cambridge 39, Massachusetts.

[3] H. W. Melville, B. Noble and W. F. Watson, *J. Polymer Sci.*, **2**, 229 (1947).

[4] Walling, THIS JOURNAL, **71**, 1930 (1949).

[5] H. W. Melville and L. Valentine, *Proc. Roy. Soc.* (*London*), **A200**, 337 (1950).

[5a] F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

[6] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

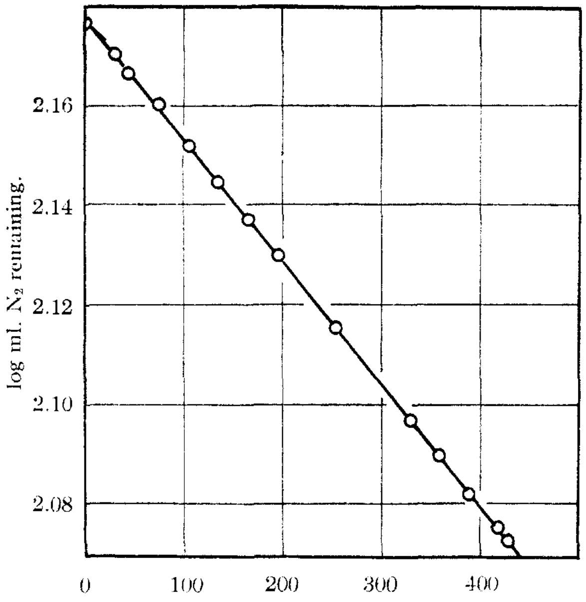

Fig. 1.—Decomposition of 2-azobis-isobutyronitrile in diethyl fumarate at 60°.

it seems highly probable that I is essentially constant in the styrene–diethyl fumarate system.

The assumption of bimolecular termination in diethyl fumarate was checked by determining the dependence of polymerization rate on initiator concentration. In Fig. 2 the rate of polymerization of diethyl fumarate is plotted against the square root of the concentration of initiator for three points of a 25-fold concentration range (0.04–1.0 g./liter). The linear plot combined with conventional kinetics indicate chain termination by bimolecular interaction of radicals. However, it is interesting to note that extrapolation of the line in Fig. 2 indicates zero rate in the presence of a small amount of catalyst. A linear plot of this sort would not be expected from either the presence of a small amount of inhibitor or a cage effect leading to the wastage of catalyst, and we are unable to advance any satisfactory explanation. However, the magnitude of the effect is such that it probably plays little role in the rate measurements at the higher concentration of catalyst employed.

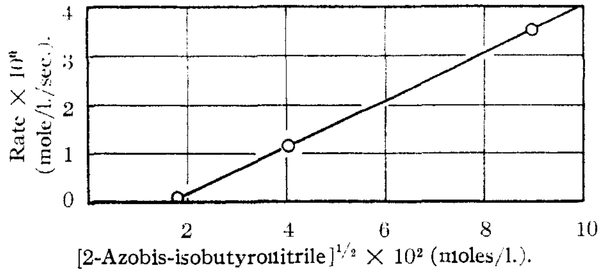

Fig. 2.—Polymerization rate of diethyl fumarate *vs.* [2-azobis-isobutyronitrile]$^{1/2}$ at 60°.

Over-all rate measurements in styrene, diethyl fumarate and four mixtures of the two, all in the presence of 1 g. per liter of 2-azobis-isobutyronitrile, are listed in Table I. Taking $\delta_2/\delta_1 = 5.66$ (from the rates of polymerization of fumarate and styrene alone), $r_1 = 0.30$ and $r_2 = 0.07$ (from copolymer composition data[7]), the values of ϕ listed in the last column may be calculated. Averaging yields $\phi = 7.75 \pm 1.5$. In Fig. 3 the data of Table I are plotted together with the calculated rate curves for $\phi = 1$ and $\phi = 7.75$. The agreement with the second curve was quite good and the data clearly show the enhanced rate of the cross termination process.

TABLE I

RATE OF COPOLYMERIZATION OF STYRENE AND DIETHYL FUMARATE AT 60° IN PRESENCE OF 1 G./L. 2-AZOBIS-ISOBUTYRONITRILE

Mole % styrene	Time, hr.	Yield, g./l.	Rate, m./l./sec. (× 10^5)	ϕ
100	2.25	50.4	5.99	
100	3.25	70.7	5.80	
85.0	2.25	51.2	5.15	6.09
85.0	3.25	76.3	5.29	
68.0	2.25	50.5	4.75	6.89
68.0	3.25	71.2	4.65	
47.2	4.5	73.9	3.38	8.84
47.2	6.0	108.9	4.10	
26.1	6.5	90.9	2.80	9.2
0.0	24.25	111.4	0.744	
0.0	7.25	32.3	.720	

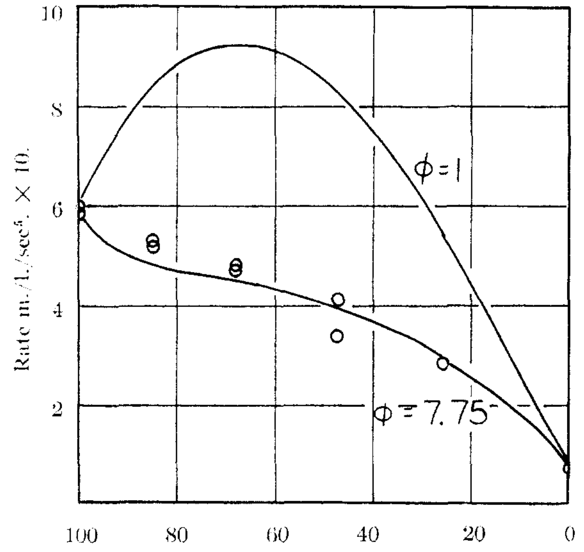

Fig. 3.—Calculated and observed rates of copolymerization of styrene–diethyl fumarate.

When ϕ is known for a system, the measurement of the over-all rates of thermal polymerization should permit the detection of any cross initiation process.[4] Table II gives the results of measurements of the rate of thermal copolymerization of four styrene–diethyl fumarate mixtures, and it will be noted that the rate of polymerization of pure fumarate is negligible. However, attempts to calculate the rate constant for thermal cross initiation from the data of Table II lead to the remarkable conclusion that the rates observed not only fail to indicate cross initiation, but are actually lower than those which would be calculated from

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(7) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs and F. R. Mayo, *ibid.*, **70**, 1519 (1948).

the known rate of chain initiation by reaction of two styrene molecules. Thus, for the experiment containing 47.2 mole % styrene, the calculated rate would be 0.63×10^{-6} m./l./sec. compared with the actual observed value of 0.168×10^{-6}. Unless the diethyl fumarate contains some inhibitor which survives rather vigorous purification techniques, such a result is very difficult to interpret; perhaps some process such as six-membered ring formation between a biradical chain containing two styrenes and one fumarate (arising from the addition of fumarate to the initial two styrene unit biradical) is involved. A similar mechanism has been suggested for the Diels–Alder reaction, and for the formation of four-membered rings when certain monomers are heated alone[8] or when tetrafluoroethylene is heated with other olefins.[9]

TABLE II

RATES OF THERMAL COPOLYMERIZATION OF STYRENE AND DIETHYL FUMARATE AT 60°

Mole % styrene	Time, hr.	Yield, g./l.	Rate $\times 10^6$, m./l./sec.
100	...	...	2.15[a]
85	161	40.2	0.60
68	161	36.8	.52
47.2	161	12.4	.168
26.1	141	2.22	.033
0	497	1.06	.003

[a] Av. value from R. A. Gregg and F. R. Mayo, THIS JOURNAL **70**, 2373 (1948).

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[8] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950); *cf.* footnote (27).

[9] D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, THIS JOURNAL, **71**, 490 (1949).

PASSAIC, N. J.

RECEIVED NOVEMBER 22, 1950

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Electrolytic Properties of Aqueous Solutions of Polyvinylpyridine Neutralized with Hydroiodic Acid

BY FREDERICK T. WALL, JOHN J. ONDREJCIN[1] AND MARIKA PIKRAMENOU

Solutions of polyvinylpyridine partially neutralized with hydrogen iodide have been electrolyzed between a silver–silver iodide cathode and a platinum anode in a transference cell separated into anode and cathode compartments by a coarse sintered glass frit. I^{131}, a radioactive isotope of iodine, was initially added as a tracer so that the net movement of the iodide ions could be determined by use of data obtained with a Geiger counter. Hydrogen ion concentrations and electrical conductivities were also measured.

A number of significant quantities were calculated using basic electrochemical equations. These included the transference number of the polyion, the equivalents of polymer transported per faraday of electricity passed through the cell, the fraction of iodide ions associated with the polyanions, and the over-all degree of ionization of the polymer. From 30 to 60% of the iodine is found to move with the cations.

Introduction

When a polymeric electrolyte is dissolved in water, it will generally ionize to some extent as any ordinary electrolyte might be expected to do. However, if the degree of polymerization is large, the per cent. of ionization appears to be small, even for salts whose monomer counterparts would be completely ionized. This apparent incomplete ionization of polymeric salts can be attributed to the very high charges that arise if appreciable ionization occurs. Such high charges give rise to ionic potential energies so great that complete ionization is energetically unfavorable.

Earlier work[2] on polyacrylic acid neutralized with sodium hydroxide showed that anywhere from 30–70% of the sodium ions might be bound to the polyanion depending upon the concentrations involved. The present investigation was carried out to learn something about the behavior of polymeric bases neutralized with a monobasic acid. For this purpose we chose the polymer of 2-vinylpyridine and hydroiodic acid. The experiments were carried out with the expectation that many of the iodide ions would be bound to the polycation and accordingly would appear to move to the cathode in an electrolysis experiment. To follow the movement of iodide it was found expedient to employ radioactive iodine, I^{131}, as a tracer.

Theory

Huizenga, Grieger and Wall[2] have already considered some of the theoretical aspects relating to electrical transference of polymeric electrolytes. Among other things, they were concerned with the effect of exchange of ions between a free state and a state in which they were bound to the polymeric ion. They showed mathematically that unless the rate of exchange is infinitely great, transference numbers cannot be simply obtained by tracer techniques unless the tracer is uniformly distributed throughout the anode and cathode compartments at the beginning of an electrolysis experiment. They further showed experimentally that in solutions of sodium polyacrylate, the rate of exchange of sodium ions between free and bound states was measurably finite. Accordingly, in our experiments dealing with polyvinylpyridinium iodide, we assumed, to be on the safe side, that the rate of exchange of iodide ions is likewise finite. Consequently all ordinary transference experiments were made with tracer uniformly distributed throughout the cell at the beginning of the experiment.

Briefly the experiments consisted of electrolyzing aqueous solutions of poly-2-vinylpyridine neutralized to varying degrees by hydrogen iodide to which some iodide tracer had been added. Since poly-2-vinylpyridine is water soluble as a basic salt in the presence of 31% or more of the equivalent amount of hydrogen iodide, the transference studies

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[1] Firestone Tire and Rubber Company Fellow 1949–1950.

[2] J. R. Huizenga, P. F. Grieger and F. T. Wall, THIS JOURNAL, **72**, 2636 (1950).